

# SOLID OXIDE FUEL CELLS FOR DIRECT UTILIZATION OF HYDROCARBONS PREPARED BY LAMINATION METHODS

Kipyung Ahn, Shung-Ik Lee, Yingyi Huang, John M. Vohs, and  
Raymond J. Gorte

Department of Chemical and Biomolecular Engineering  
University of Pennsylvania, Philadelphia, PA 19104 USA

## Introduction

Solid oxide fuel cells (SOFCs) show great promise for power generation in a wide range of applications. Because they are based on a ceramic, oxygen ion-conducting membrane, a SOFC can theoretically operate on any combustible fuel, including CO [1,2] and hydrocarbons [3-5], allowing them to be used with fuels that are readily available today. However, in order to operate on hydrocarbon fuels, it is necessary to choose the materials that are used in the anode with great care. For example, Ni, which is commonly used in anodes on fuel cells that utilize  $H_2$ , tends to form carbon fibers in the presence of hydrocarbons.

In general, the first step in fabricating SOFC electrodes involves high-temperature sintering of mixed oxides including electrolyte materials. This approach limits the choice of materials that can be used for the electrode since the oxides may decompose or undergo unwanted solid-state reactions at high temperatures. Therefore, alternative methods are required for preparation of electrode composites in order to incorporate a wide range of materials that may have superior catalytic or current collection properties.

Recent work in our laboratory has demonstrated that it is possible to prepare SOFC electrodes from a wide range of materials by using low-temperature methods in which the electronically conductive component is added by impregnation with soluble salts to a porous matrix of the electrolyte material [6,7]. The primary advantage of producing electrodes in this manner is that the porous matrix can be sintered together with the electrolyte to very high temperatures before the active component is added, allowing the processing temperatures for the two components to be decoupled.

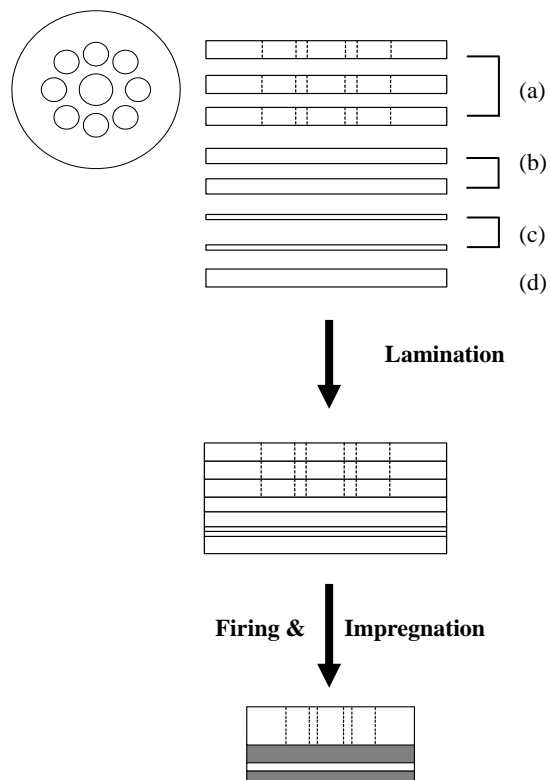
In this paper, we describe the fabrication of SOFCs with high-performance electrodes, having controlled structures and capable of producing electrons directly from hydrocarbon fuels, without reforming. These SOFCs were produced using a single, high-temperature sintering step in which the initial structure consists of a dense layer of YSZ separating two porous layers and is produced by lamination of green ceramic tapes. An additional layer with holes was laminated on top of one of the porous layers to provide mechanical strength and rigidity.

## Experimental

The YSZ components of the fuel cells were fabricated using YSZ green tapes prepared by tape casting. The YSZ powder (8 mol%  $Y_2O_3$ , TZ-8Y, Tosoh) used in the tapes was initially ball milled for 20 h with water and a dispersant (Darvan C, R.T. Vanderbilt Company,

Inc.) to break up agglomerates. Emulsion-type binder solutions (Duramax HA-12 and B-1000, Rohm and Haas) were added to the slurry and mixed by stirring for 24 h before casting. Pyrolyzable pore formers such as graphite (325 mesh, Alfa Aesee) and polystyrene-divinylbenzene (200-400 mesh, Alfa Aesee) were added together with the YSZ powder to the tapes used in the electrodes in order to introduce porosity.

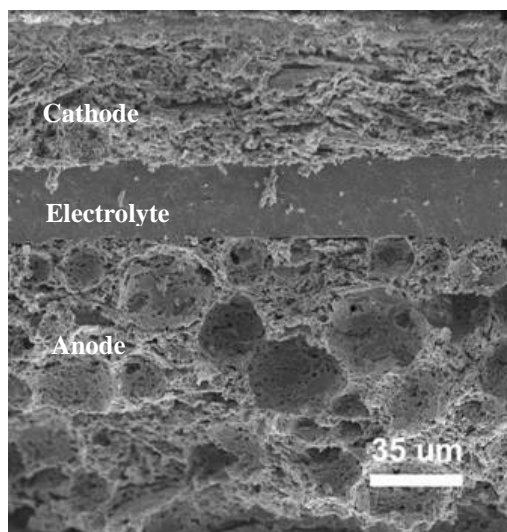
An SOFC was prepared by lamination of various green tapes using a uniaxial hydraulic press equipped with heating platens (Carver Inc.). To improve the mechanical strength of the cell a relatively thick YSZ support layer was used. This support layer was in turn laminated together with the layers that would make up the cathode, electrolyte, and anode, as shown schematically in Fig. 1. The thicknesses of the anode, cathode, and electrolyte layers after firing were 100  $\mu m$ , 60  $\mu m$ , and 25  $\mu m$ , respectively. The anode layers contained a mixture of graphite and polystyrene-divinylbenzene pore formers, while the cathode layer contained only graphite. After lamination, the tapes were fired at 1823 K for 4 h. The anode and cathode composites were fabricated using impregnation of the porous YSZ matrices with aqueous solutions. The final composition of the tested cell was 15 wt%  $CeO_2$ , 21 wt% Cu, 9 wt% Co for the anode and 40 wt%  $La_{0.6}Sr_{0.4}CoO_3$  for the cathode.



**Figure 1.** Schematic of the fabrication procedure for the laminated cells. (a) support layer, (b) YSZ + graphite + polystyrene divinylbenzene, (c) dense YSZ, (d) YSZ + graphite

## Results and Discussion

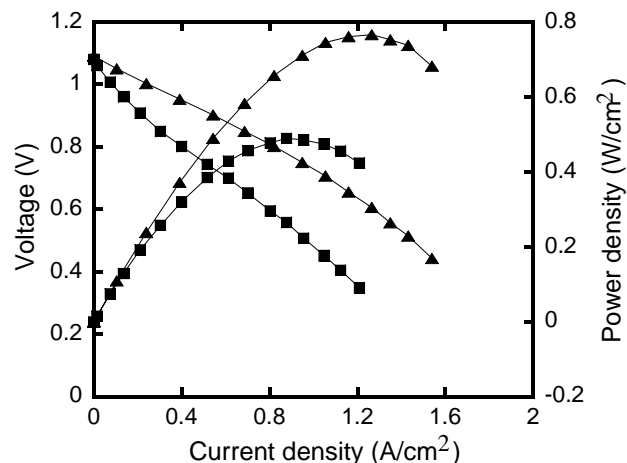
Figure 2 shows an SEM image of a cross section near the electrolyte interface of the cell that was prepared by the lamination process shown in Figure 1, prior to the impregnation of the anode and cathode materials. Only small pores in the range of 1 to 2  $\mu\text{m}$  in diameter were present in the cathode layer, while the anode layer had large pores with a size of about 20  $\mu\text{m}$  in addition to the small pores. The small and large pores in the electrodes were introduced by graphite and polystyrene-divinylbenzene pore formers, respectively. The porosities of the anode and cathode porous layers were 65 % and 70%, respectively. The cell consists of three support layers, two anode layers, two electrolyte layers and a cathode layer. The micrograph demonstrates that there was good contact between the electrolyte layer and the porous YSZ electrode layers, with no evidence for cavities between layers. This result shows the microstructure of the electrodes can be engineered by laminating several layers having different microstructures. Furthermore, the dense support layer was found to provide mechanical strength to the cell so that thin electrolytes and electrodes can be used. This indicates some of the issues encountered in electrolyte or electrode supported cells can be avoided by using support layers [8].



**Figure 2.** SEM image of the YSZ structure used for making the cell in this study

In previous work, it was shown that  $\text{Cu}_{0.7}\text{Co}_{0.3}$  bimetallic mixtures are stable towards carbon fiber formation in the presence of hydrocarbon fuels, even though Cu and Co do not form an alloy [9]. It appears that Cu coats the surface of the Co crystallites, suppressing carbon formation. However, the presence of the Co within the anode still enhances the electrochemical performance. The performance of the  $\text{Cu}_{0.7}\text{Co}_{0.3}\text{-CeO}_2\text{-YSZ|YSZ|LSCo-YSZ}$  cell in  $\text{H}_2$  and n-butane at 1023 K is shown in Figure 3. For operation using  $\text{H}_2$  with 3 vol%  $\text{H}_2\text{O}$ , the open-circuit voltages (OCV) were close to the theoretical, Nernst potential of 1.1 V. A maximum power density of 770  $\text{mW}/\text{cm}^2$

was achieved at 1023 K. For n-butane, the OCV was slightly lower than predicted by the Nernst potentials,  $\sim 1.12$  V. The maximum power density was 490  $\text{mW}/\text{cm}^2$  at 1023 K, lower than that with  $\text{H}_2$ , showing that the chemical oxidation reaction must partially limit performance.



**Figure 3.** Cell performance curves at 1023 K in (▲)  $\text{H}_2$  and (■) n-butane

## Conclusions

We have demonstrated a new fabrication method for SOFCs for direct utilization of hydrocarbon fuels. The method involved lamination of ceramic tapes prepared by tape casting with or without pore formers and a single step firing, followed by impregnation of nitrate solutions. Utilization of perforated support layers allowed SOFCs consisting of thin electrolytes and thin electrodes to be fabricated, providing flexibility in designing cell structure.

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